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Trace Organometallics in Water

by

Nancy Simon, Andrew J. Weinoir, and M. J. Aldridge

June 1978

to

U.S. Army Mobility Equipment Research

and Development Command

Fort Belvoir, Virginia

Prepared by

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20. Abstract (continued)

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This led to our second approach, the development of a gas chromatographic method which would eliminate the extraction or preconcentration step. Aue and Hill (3) had reported the development of a hydrogen-rich flame ionization detector that was both sensitive and selective in the lower nanogram ranges for iron, tin and lead compounds. The latter half of this research project was concerned with numerous modifications to their design of the Hydrogen Atmosphere Flame Ionization Detector (HAFID) in an effort to make it applicable for the determination of trace amounts of tetra-n-butyl tin and tributyltin chloride in water solutions heavily contaminated with hydrocarbons without the necessity of a preconcentration step.

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I ACKNOWLEDGEMENT

II ABSTRACT

The objective of this research was to develop sensitive and accurate methods for the determination of organometallic compounds of copper, mercury, and tin in water. Tin was given top priority because of the marked increase in industrial production of organotin compounds during the last decade.

Organotin compounds are soluble in water at levels so low that our first approach was devoted to the development of reproducible methods for their extraction and concentration prior to quantification by atomic absorption spectrophotometry. Instrumental conditions suitable for each solvent had to be determined and the sensitivity and reproducibility of the atomic absorption data depended upon the proper choice of the drying, charring, and atomizing temperatures. Because of the high volatility of tetra-n-butyl tin (b.p. 145°C) and the low volatility of tin (b.p. 2270°C) the sensitivity and reproducibility of the atomic absorption data were not satisfactory. In order to completely atomize the tin, the graphite furnace had to be heated to the maximum temperature, 2700°C. Lower temperatures left a residue of tin which subsequently created erroneously high results.

This led to our second approach, the development of a gas chromatographic method which would eliminate the extraction or preconcentration step. Aue and Hill (3) had reported the development of a hydrogen-rich flame ionization detector that was both sensitive and selective in the lower nanogram ranges for iron, tin and lead compounds. The latter half of this research project was concerned

with numerous modifications to their design of the Hydrogen Atmosphere Flame Ionization Detector (HAFID) in an effort to make it applicable for the determination of trace amounts of tetra-n-butyl tin and tributyl tin chloride in water solutions heavily contaminated with hydrocarbons without the necessity of a preconcentration step.

III INTRODUCTION

Modern technology has put many materials to use which, while serving man, are a threat to his health and safety. Organometallic compounds are used in general as insecticides, pesticides, fungicides, molluskicides, anthelmintics, and bactericides. More specifically, they are used in antifouling paint, as wood preservatives, in moth proofing, in seed dressings, and as rodent repellents (8, 23, 25, 36, 42, 43). When these materials spread in the environment they are highly toxic, at very small concentrations, to plant and animal life. Also, the inorganic metal ions in water, which at low concentrations can be toxic to to marine life, may be converted by biological transformations to organic compounds of much greater toxicity (6). Organometallic compounds of copper, mercury and tin are of particular concern.

Bonding affects the toxicity of organometallic compounds. Alkyl organometallic compounds are more toxic than aromatic organometallic compounds. Organotin compounds with three carbon-tin bonds are more toxic than those with 1, 2, or 4 carbon-tin bonds (45, 50). Tributyltin oxide is lethal to aquatic microorganisms and fish at 1 to 3 parts per billion in water (25, 26, 40). The level for acute toxicity to warm-blooded animals (rats) is 148 - 234 mg/kg (25, 42). Other organometallic compounds are toxic in much smaller quantities.

In general, the most important effect of organometallic compounds on an animal is on its central nervous system (36). There may be other effects, as with bis-(tributyltin) oxide which attacks

the gastrointestinal system (36), the liver (36, 50), and the blood
index (8) as well as the central and vegetative nervous system (8, 36).

Organometallic materials can be decomposed by ultraviolet
light but their presence in the environment is persistent (14, 49),
and strong oxidants are needed to remove them from water samples (25).

Due to the wide distribution of organometallic compounds,
and their high toxicity, it is evident that methods are needed for
extracting, identifying and quantifying these materials in both
fresh and marine water. There are no methods currently developed to
accomplish this task (15). The methods developed should be specific
for the compound under investigation, reliable, rapid, versatile with
respect to sample matrix and economical both in terms of equipment
and manpower. Public concern about the environment has originated
from, been precipitated by, or made possible through the development
of sensitive, accurate analytical methods for contaminants of the
atmosphere (3). The setting and enforcement of industrial and
domestic waste discharge standards is dependent on the methods of
analysis for pollutants.

Selection of the proposed routes of analyses are based on
literature references to compounds similar to the organometallics
of interest. Organic compounds with low water solubility, such as
pesticides, can be extracted from water using a resin, and removed
from the resin with an organic solvent as the eluant (38).

The Rohm and Haas Company produces a line of Amberlite resins
which are copolymers of styrene and divinylbenzene with macroreticular
structure. Two of these resins, XAD-2 and XAD-4, are described in the

literature as being very efficient absorbents for neutral and polar

organic materials.

Resin	Porosity vol %	cm³/gm	Surface Area m/gm	Avg Pore Diameter	Skeletal Density gm/cm³	True Density	Mesh
XAD-2	42	0.69	330	90	1.08	1.03	20 - 50
XAD-4	57	0.99	750	50	1.09	1.02	20 - 50

In general, XAD-2 is used for removal of neutral and slightly

polar organic compounds from water (10, 11, 22, 31, 44), and sometimes

chloro-pesticides (27, 41). XAD-4 is more often the choice for

removal of pesticides (38). In either case the resin does not absorb

strongly ionic salts such as sodium chloride and potassium chloride (10).

This is of particular importance when working with marine samples.

The eluant from the resin will contain the organometallic compounds

and not the inorganic metallic compounds.

The eluant must be appropriate for use in both atomic

absorption spectrophotometry and gas chromatographic analyses. An

alcohol, such as ethanol, is suitable for both.

The eluant may be analyzed using atomic absorption spectro-

photometry to determine the concentration of the metallic component

of the organometallic compound (29). Using electrodeless discharge

lamps to decrease background noise (7), organic solvents to increase

sensitivity (2), and the heated graphite atomizer, metals can be

determined at the parts per billion level (28). At the low

concentrations present in the water samples of interest, it is

mandatory that a graphite atomizer (furnace) be used rather than a

flame. Recent advances using the graphite furnace permit the

determination of volatile metals such as mercury and tin using matrix

modification (19, 28, 35). The high salt concentration of marine samples may be handled with furnace adaptation (18) or matrix modifications (1, 20).

Gas chromatography can be used to analyze the eluant to determine the concentration of organometallic compounds (9, 12, 21, 34). A modified flame ionization detector can be used for identification as well as for quantification of organotin and organomercury compounds (3, 4, 17, 20). There is some indication in the literature that the presence of more than one organometallic compound (for example, organomercury and organotin) increases the sensitivity of the gas chromatographic method.

The mass spectra of three mercury alkyls have been recorded, namely, $Hg(CH_3)_2$, $Hg(C_2H_5)_2$ and $Hg(n-C_4H_9)_2$ (53).

The mass spectra of tetramethyl tin was also recorded by Dr. Vernon Dibler at the National Bureau of Standards (54).

The objective of our research was to develop a sensitive and accurate method for the determination of the organometallic compounds of copper, mercury and tin in water.

IV EXPERIMENTAL

A. Atomic Absorption Spectrophotometry

There was some delay in obtaining the organometallic tin compounds selected for study, so preliminary work was done with tetravinyl tin [$(CHCH_2)_4Sn$].

A comparison was made of acidified water, acidified ethanol, and 100% ethanol as suitable solvents for use with tetravinyl tin and the flame atomic absorption spectrophotometer.

Tetravinyl tin dissolves readily in all three solvents. The absorbance values in Table 1 were obtained using a Varian Model 1200 Atomic Absorption Spectrophotometer with an air-acetylene flame and a wavelength setting of 224.7 A.

Table 1. Concentration in ppm Sn

	50	20	10
0.1 N HCl/H_2O	.053	.024	.011
0.1 N HCl/EtOH	.027	.014	.005
100% EtOH	.053	.029	.015

There was no apparent difference between 0.1 N HCl in water and 100% ethanol as a solvent for tetravinyl tin.

In an effort to increase the sensitivity of the method, lithium chloride (LiCl) was added at 1000 ppm levels to 0.1 N HCl/H_2O and 100% ethanol solutions. The absorbance values obtained seemed somewhat more steady with the addition of LiCl.

Table 2. Concentration in ppm Sn with

Addition of 1000 ppm LiCl

	50	20	10
0.1 N HCl/H_2O	.077	.026	.013
0.1 N HCl/EtOH	.042	.012	.003
100% EtOH	.053	.022	.011

To optimize operating conditions several changes were tried on the atomic absorption spectrophotometers being used. These included the Varian Techtron Model 1200 and the Perkin Elmer Models 503 and 603.

Various gas mixtures were tried including nitrous oxide-acetylene, nitrous oxide-air, and acetylene. The data in Table 3 indicate there is no difference among the mixtures when the amount of tin in the organic form is being determined.

Table 3. Concentration in μg Sn/ml

in Various Gas Mixtures

Sn	N_2O-C_2H_2	N_2O-Air	Air-C_2H_2
.46	.0185	.019	.0190
.93	.0315	.0315	.0315
1.86	.0560	.0560	.056

When a three slot burner with air and acetylene was used with the Perkin Elmer Model 503, the absorbance readings for tin were

significantly depressed. A comparison of wavelengths 224.7 A and
286 A showed 224.7 A to be preferred.

Table 4. Values Using a Three Slot Burner

Concentration μg Sn/ml	286 A	224.7 A
46	.026	.037
93	.046	.077
186	.100	.150

The compounds obtained for study and the letter used to
designate each throughout this work are:

bis(tributyltin)oxide	$(C_4H_5)_3Sn_2O$	A
tetra-n-butyltin	$Sn(C_4H_9)_4$	B
dibutyltin oxide	$(C_4H_9)_2SnO$	C

The concentrations of all solutions of these compounds are calculated
on the basis of milligrams of tin per liter. All solutions were
prepared with weighed samples. Compounds A and B are very viscous
and a volume measurement used in conjunction with a value for
density leads to inaccuracies. In general, water solutions, after
the initial experiment described below, were prepared by dissolving
the compound in approximately 10 ml of ethanol and then making the
ethanol up to one liter with water.

Various solvents were tried when the three compounds became
available. These included hot water, 100% ethanol, 20% ethanol,
100% acetone, and 20% acetone.

Table 5 gives approximate concentrations of organometallic tin in solution based on inorganic tin standards. (See graph 1.) Only A dissolved in hot water or 100% ethanol appeared clear after 5 days. All other solutions were cloudy or had a visible precipitate.

This experiment suggested that varying the concentration of organic solvent in water might influence the sensitivity of the atomic absorption method. Table 6 indicates that both very high and very low ratios of water to organic solvent give better sensitivity but that a higher percentage of organic solvent provides a more stable solution.

Graphs 2 and 3 give standard curves which are characteristic of bis(tributyltin)oxide (compound A) in 100% ethanol. Absorbance values were obtained using the Perkin Elmer Model 603 Spectrophotometer with graphite furnace at a wavelength of 224.7 A.

Due to the very low levels of organometallic tin expected in the water samples to be analyzed, the graphite furnace was chosen over the flame method because the graphite furnace has the advantage of greater sensitivity. With nitrogen as the sheathing gas, the expected sensitivity for tin (inorganic) is 40 pg/.0035 absorbance units and for argon it is 50 pg/.0030 absorbance units. A flow rate of 0.5 1/min is the maximum flow that can be used without losing sensitivity. The flow interrupt mode also helps increase sensitivity.

A program for drying, charring, and atomizing the organometallic compounds was developed based on the following considerations: Butylated organometallic tin compounds have relatively low boiling points. The boiling point for bis(tributyltin)

TABLE 5

Solvent Effects

	Solution	Approximate Concentration Sn (ppm)	Concentration Sn from AA (ppm)
A = bis(tributyltin)oxide	A_0	50	20
	A_1	500	184
	A_2	500	420
	A_3	200	31
	A_4	200	160
B = tetra-n-butyltin	B_0	40	33
	B_1	160	80
	B_2	160	115
	B_3	160	47
	B_4	160	149

Subscripts: 0   hot water
1   100% ethanol
2   20% ethanol
3   100% acetone
4   20% acetone

Table 6

Absorption of Compounds A, B, and C with Variation

of the Proportion of Organic Solvent to Water

Compound (ppm)	Ethanol (%)	Initial Absorbance	Absorbance After 5 Days
A 176	15	.378	.366
176	10	.363	.057
176	5	.416	.076
46	100	.164	.169
93	100	.319	.369
186	100	.592	.693
B 156	15	.063	.028
156	10	.088	.015
156	5	.141	.010
C 76	15	.016	.006
228	10	.023	.013
166	5	.025	.001

A = bis(tributyltin)oxide

B = tetra-n-butyltin

C = dibutyltin oxide

GRAPH 1

Inorganic Standards 20% EtOH	
ppm Sn	Absorbance
10	.008
20	.022
50	.050
100	.105

Y = A + B*X

E +2

A = 0.97923269785B

B = 962.202563981

R-SQUARE = 0.998530619968

RES ERROR 3.59998107763

MAX(ABS(RESIDUAL)) 2.14768910545

ESTIMATE FOR EQUATION : Y = A + B*X

A_0 X=.020 20.2232839775

A_1 X=.191 184.75992418

A_2 X=.409 470.534083921

A_3 X=.032 31.7697147453

A_4 X=.166 160.704858319

B_0 X=.033 32.7319173092

B_1 X=.082 79.8798429443

B_2 X=.118 114.519135248

B_3 X=.048 47.164955769

B_4 X=.154 149.158427551

X=

GRAPH 2

X,Y = .164,46.5
X,Y = .319,93
X,Y = .592,186

E -1

+2.00   +3.00   +4.00

E
+2
+1.80

+1.60

+1.40

+1.20

+1.00

+0.80

+0.60

+0.40

Y = A + B*X

A =
-8.8965262052

B =
327.618212666

R-SQUARE =
0.99895875905

RES ERROR
10.5066418091

MAX(ABS(RESIDUAL))
2.61368363515

GRAPH 3

X,Y = .169,46.5
X,Y = .369,93
X,Y = .693,186

E -1

+2.00   +3.00   +4.00   +5.00

E +2
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40

Y = A + B*X

A =
-1.55741838914

B =
268.214667073

R-SQUARE =
0.997849914467

RES ERROR
29.7678380749

MAX(ABS(RESIDUAL))
4.41379376096

oxide is 254°C and for tetra-n-butyltin is 145°C. It was decided to decrease loss through volatilization by eliminating the drying step. During the charring step a temperature of more the 110°C caused a significant loss of the tin compounds. Simply air drying the sample for 30 to 60 seconds did not give reproducible results. Charring at 110°C for 30 to 60 seconds, depending on the volatility of the solvent, gave good results. The charring time at 110°C for toluene is 60 sec, for hexane 30 sec, and for ethanol 10 sec. Perkin Elmer suggests the highest temperature obtainable (2700°C) as the atomizing temperature for tin. The organometallic tin compound will leave a residue in the graphite tube if a lower temperature is used. This may be seen by observing the absorbance readings evident when the furnace is heated to maximum after an organometallic tin sample is run at less than 2700°C.

In order to better deal with the salt interferences from marine samples, ammonium nitrate was added to the samples. The ammonium chloride formed was reported to volatilize. This approach did not help since the high temperature needed to remove the ammonium chloride also caused a loss of organometallic compounds.

Having developed a satisfactory procedure for use with the atomic absorption spectrophotometer with a graphite furnace, an evaluation of macroreticular resins for removal and concentration of organometallic compounds from water was initiated.

Work with the XAD-2 resin indicated that it will adsorb bis(tributyltin)oxide (A). Approximately 10 g of XAD-2 resin was used with a flow rate of 10 ml/min. (Flow rate suggested by the work of A. Welebir.)

Total organic carbon (TOC) was run on samples 1 and 2 (Table 7). In both cases the TOC values were increased by approximately 30% when comparing the original solutions with the last 25 ml of effluent. This may mean that some of the resin is filtering through the glass wool or may be a result of poor retention from more concentrated solutions.

When determining the concentrations of Sn with the AA using water-ethanol solutions, the standards must have the same percentage of water and ethanol. This adjustment must be made after the total volume of eluant is determined. (Some water from the column is added to the ethanol.) A solution of 95% ethanol will have an absorbance of approximately 5% greater than a 100% ethanol solution. Addition of LiCl (1000 ppm) at near 100% concentrations of ethanol improve the precision of the AA data.

The effluents were found to have considerable amounts of tin in them (1 μg/ml). This suggests that the 10 ml/min flow rate is too rapid for good sorption by the resin.

Slower flow rates (1 and 0.4 ml/min) and the addition of an inorganic salt ($SnSO_4$) were tried using the XAD-4 resin (10 gm) and bis(tri-n-butyltin)oxide (compound A). Table 8 shows the results obtained using a Perkin Elmer Model 370 Atomic Absorption Spectrophotometer with a graphite furnace.

There was no tin in evidence in the effluent of any of these solutions (Table 8). This indicates that compound A was retained on the column and that the inorganic tin will not come through the resin under these conditions. At the working pH, the tin apparently hydrolyzes and is filtered out of the solution by the glass wool and resin.

Table 7

Sample	Amount of Solution Run Through Column/Total Volume (amount compound A)	Theoretical Concentration Sn on Column	ml Eluant 100% Ethanol	Amount Sn Removed	% of Theoretical Total on Column
1	200/1000(10 µl)	1.86 mg	100	.150 mg	8%
2	250/1000(20 µl)	4.65 mg	100	.43 mg	9%
3	250/1000(20 µl)	2.3 mg	25	.45 mg	19%
4	500/1000(20 µl)	4.65 mg	25	110.0 mg	22%
5	500/1000(10 µl)	2.3 mg	50	.9 mg	39%

Table 8

Amount of Solution Run Through Column/Total Volume (Amount of Compound A)	Flow Rate (ml/min)	Amount Ethanol Eluant (ml)	Amount Sn on Column* (μg)	Amount Sn Eluted (μg)	Sn Removed (%)
500/1000 (10 μl)	1.0	50	650	500	77
500/1000 (10 μl)	0.4	50	650	650	100
500/1000 (10 μl) + 10 μg/ml Sn as SnSO$_4$	0.4	50	650	500 500	77

*The concentration of Sn actually in solution was 0.65 μg/ml (14% of the theoretical value of 4.65 μg/ml). The difference most likely is due to sorption on the glass surface.

TOC data were obtained for samples containing approximately 4 µg/ml of Sn before and after flowing through XAD-4 resin at 10 ml/min. The TOC decreased 10%. The TOC instrument at Ft. Belvoir is not sensitive enough to give dependable results with samples having a high dilution factor. The presence of ethanol in the samples makes dilution necessary.

In Table 9 the data compare the resins XAD-2 and XAD-4 at flow rates of 0.4 ml/min and 1.0 ml/min using Potomac River and Chesapeake Bay waters. All solutions contain 10 µl of bis(tri-n-butyltin)oxide (A) per 1000 ml. Absolute ethanol (50 ml) was used to elute the organotin compound from all columns. These data indicate that:

1. Only about 0.5 mg of Sn as the organometallic compound A is soluble in 1 liter of water. This is about 11% of the theoretical 4.6 mg present in 10 µl of compound A.

2. The data, in general, indicate that XAD-2 may be more efficient than XAD-4.

3. There appears to be no difference between the flow rates of 0.4 and 1.0 ml/min.

Observation: In addition to the somewhat better efficiency obtained with XAD-2 as compared with XAD-4 resin, there appear to be other bases for the choice of XAD-2. The literature cites the use of XAD-2 as a resin for selectively removing polar organic metabolites from biological samples. Also, when ethanol is added to XAD-4, the resin swells approximately 25% and changes from a pale yellow (in water) to a bright amber color. There is no apparent change in the

Table 9

	Amount of Solution Run Through Column	Flow Rate (ml/min)	Calculated Sn on Column	Calculated Amount Sn Eluted	Concentration of Sn in Effluent
XAD-2 Potomac River	400/1000	0.4	0.2 mg	0.5 mg	0
	400/1000	1.0	0.2	0.9	0
Chesapeake Bay	400/1000	0.4	0.02 mg	n.c.	n.c.
	400/1000	1.0	0.02	0.2 mg	n.c.
XAD-4 Potomac River	400/1000	0.4	0.21 mg	n.c.	-
	400/1000	1.0	0.21	n.c.	-
Chesapeake Bay	400/1000	0.5	0.03 mg	n.c.	n.c.
Cheseapeake Bay	400/1000	1.0	0.03	n.c.	-

XAD-2 resin upon addition of ethanol.

The use of macroreticular resins will adequately remove organometallic compounds from water and allow quantification with atomic absorption spectrophotometry but it is not amenable to identification of the compounds since the formation of metal chlorides is encouraged by the use of a mixture of ethanol and hydrochloric acid.
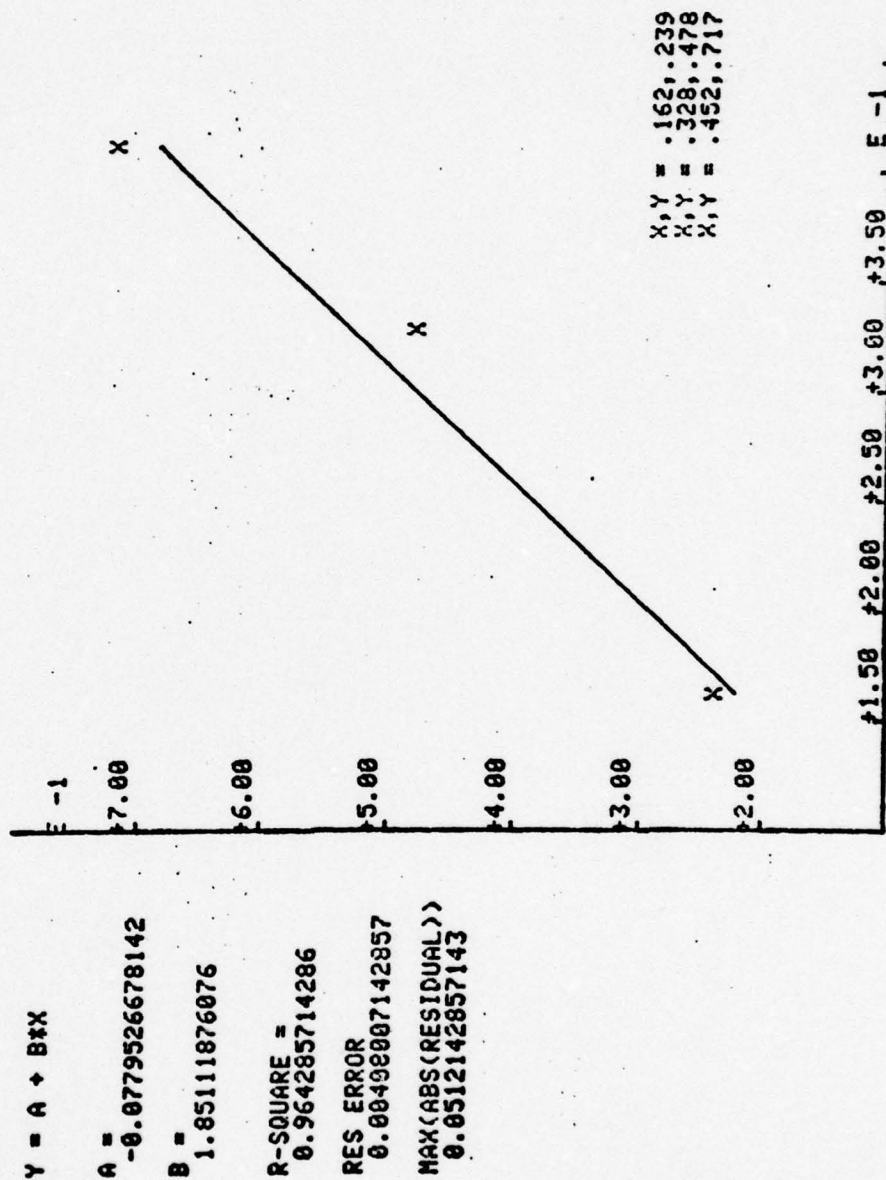
Extraction with organic solvents was the second approach to the removal of organometallic compounds from water. Among the solvents tried were methyl isobutyl ketone, chloroform, toluene and hexane. Methyl isobutyl ketone and chloroform were poor solvents for use with the graphite furnace. Both have large, erratic absorbances for the blanks. Both hexane and toluene are excellent solvents for organometallic compounds and both appear, from preliminary work, to be equally good extractants.

A comparison was made of hexane and toluene and a method developed for evaluating them. In order to obtain comparable standards and samples, the standards needed to be shaken with water in the same proportions as the samples being studied. Just as in the work with ethanol and acetone, the presence of water in the mixture changed the sensitivity of the atomic absorption spectrophotometer.

Toluene was selected as the preferred extractant. Graphs 4 and 5 show standard curves for each. Toluene produced an absorbance to unit concentration ratio of .82 with bis(tri-n-butyltin)oxide and hexane produced a ratio of .68. The standard curves of toluene were
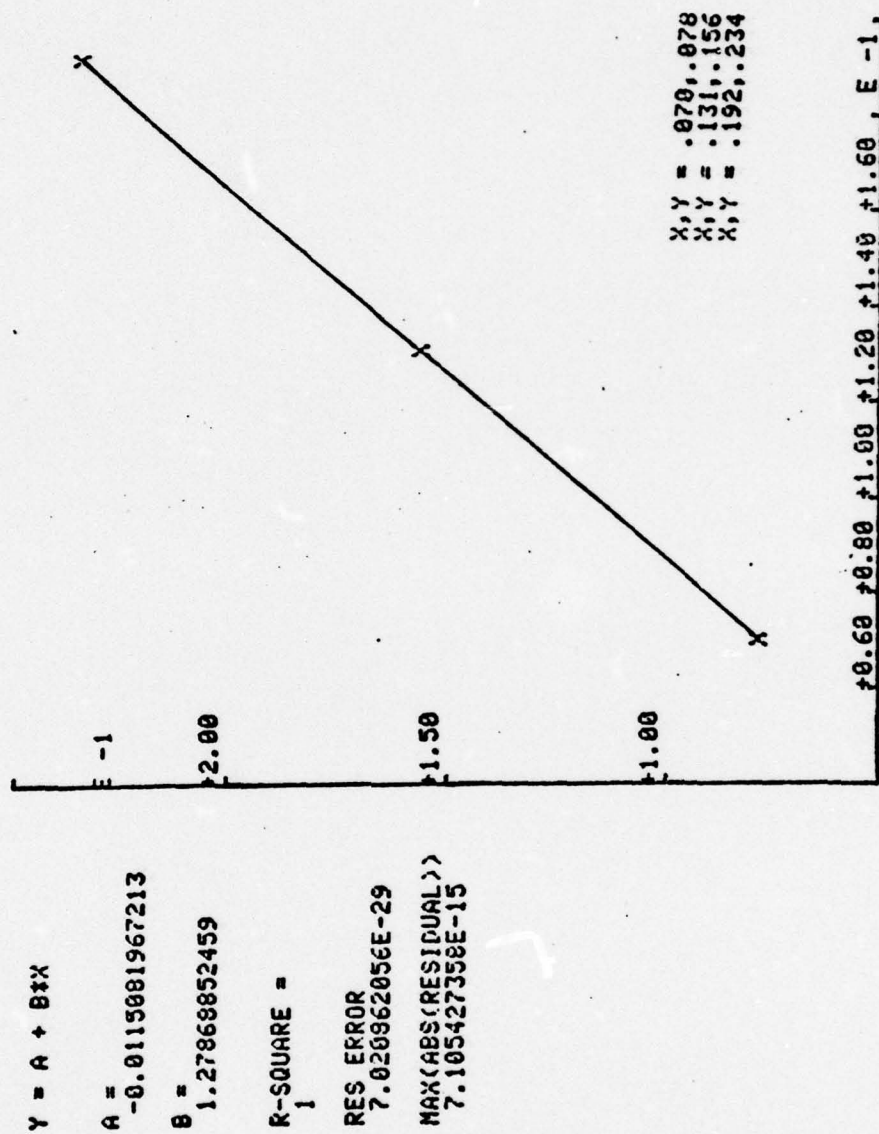
GRAPH 4

Bis(tributyltin)oxide in hexane

X,Y = .162,.239
X,Y = .328,.478
X,Y = .452,.717

$Y = A + B*X$

A =
-0.0779526678142

B =
1.85111876076

R-SQUARE =
0.964285714286

RES ERROR
0.00490007142857

MAX(ABS(RESIDUAL))
0.0512142857143

GRAPH 5

Bis(tributyltin)oxide in toluene

X,Y = .070,.078
X,Y = .131,.156
X,Y = .192,.234

E -1

↑0.60 ↑0.80 ↑1.00 ↑1.20 ↑1.40 ↑1.60 , E -1

E -1

2.00

1.50

1.00

Y = A + B*X

A =
-0.0115081967213

B =
1.27868852459

R-SQUARE =
1

RES ERROR
7.02096205 6E-29

MAX(ABS(RESIDUAL))
7.105427358E-15

more reproducible. It is less volatile than hexane which leads to less concern about concentration variation due to evaporation. Toluene is a suitable solvent for use with a gas chromatograph which makes it valuable for use in our projected goal of identifying the organometallic compounds using a modified flame ionization detector.

Suggestions for further work:

1. Check contamination from Eppendorf Pipette tips.

2. Redistill solvents.

3. Clean all glassware with extractant.

4. Leach metals from storage bottles by letting them sit containing water for a period of time.

5. Filter seawater.

6. Ionization interferences can be helped by adding an easily ionizable ion such as sodium.

7. The method of additions may be used to overcome matrix interferences.

8. Teflon containers and "glassware" should be used to help avoid sorption of the materials.
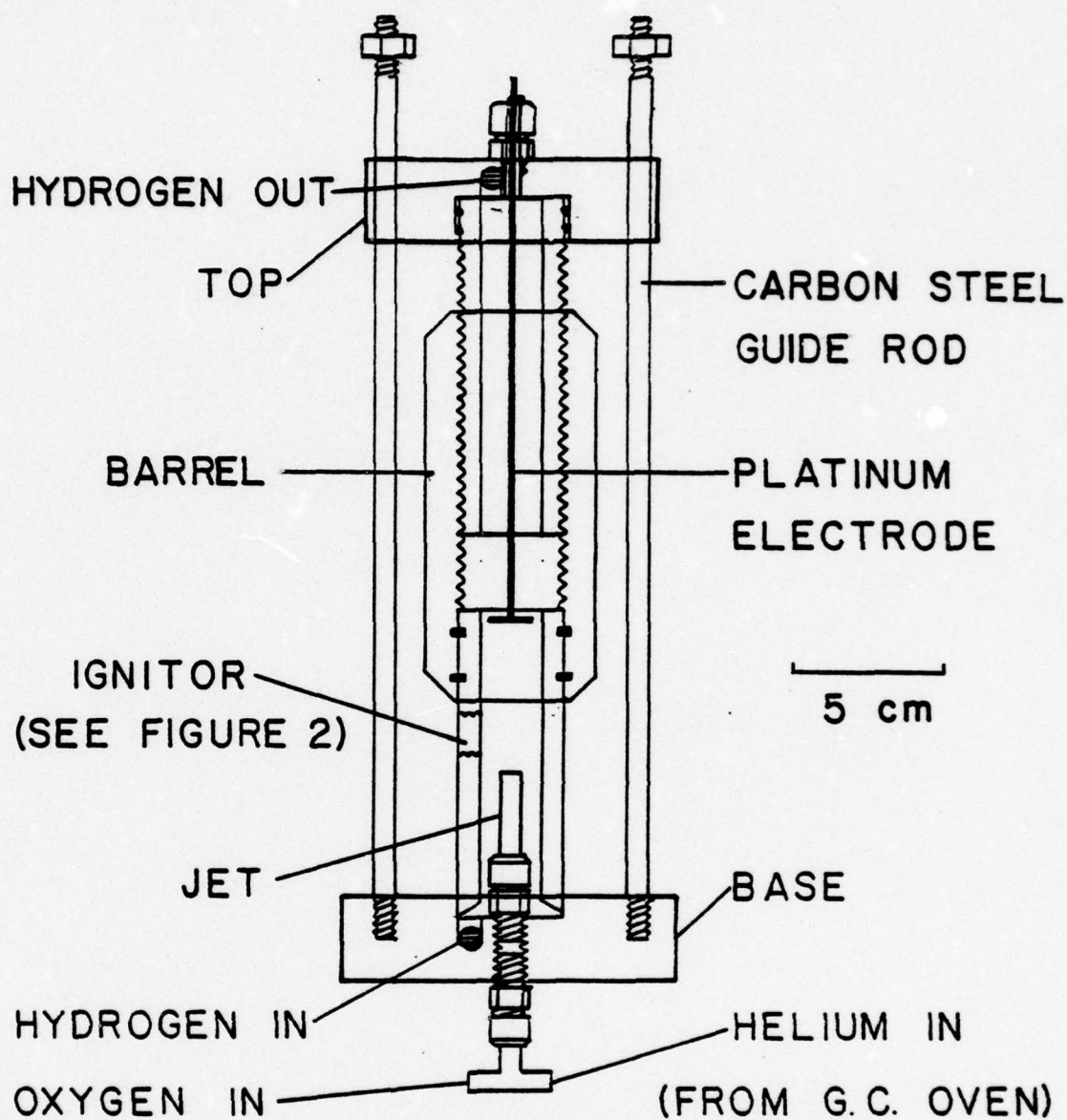
B. <u>Hydrogen Atmosphere Flame Ionization Detector (HAFID)</u>

1. Detector Design

The primary consideration in improving the original detector designed by Aue and Hill (3) was a reduction in the volume of the detector barrel. The orginal design was estimated to have an internal volume of about 800 cm^3, and the revised detector, while having approximately the same height, had a reduced inside diameter of 19 mm. This resulted in a 15% decrease in volume. The reasons for this reduction were twofold: a) to reduce the magnitude of potentially violent explosions which were found to occur with the original model, and b) to attempt to reduce the large amount of hydrogen required by that model (ca. 1 liter min^{-1}). This alteration in size led to many drastic changes in the original design.

The barrel, base, and top of the detector were all machined from solid aluminum stock, an endeavor requiring some forty hours of labor. Aluminum was chosen over stainless steel due to its greater workability and lower cost. Gas line connections were made using stainless steel Swagelok fittings.

The barrel consisted of three sections, two of which were threaded to allow continual adjustment of the platinum electrode height from the jet (see Figure 1). The importance of this adjustment was stressed in the original work. No continual adjustment was incorporated in our design, however, but aluminum spacers were substituted for the threaded devices. The assembled barrel was threaded on the lower end to allow a secure connection to the detector base. The top was held in place using the friction supplied

FIGURE 1. THE HYDROGEN ATMOSPHERE
FLAME IONIZATION DETECTOR.

by two silicone rubber O-rings. This was designed to prevent damage to the detector in the event of an explosion while holding the upper section of the barrel stationary during rotation of the center section.

Two high-carbon steel guide rods (1/4" o.d.) were threaded at both ends. One end of each rod was attached to the detector base, and the other was fitted with two hexagonal nuts. These rods prevented rotation of the top of the detector while adjustments to height were being made and they also served to prevent the top from blowing off and being damaged in the event of an explosion. The height of the assembled detector was about 35 cm.

The inside of the detector was coated with a solution of SE-30 silicone rubber gum in chloroform to insulate the platinum electrode from the barrel wall. Without this treatment, a lower response on the detector would be observed, as described in the work by Aue and Hill. In their work, however, the column was allowed to bleed into the detector (OV-17 silicone rubber).

In order to prevent uneven back pressure in the hydrogen effluent line caused by water condensation, a trap was incorporated in the line. At first, a 1 liter Erlenmeyer flask (Pyrex glass) was used. The first explosion that occurred proved the dangers of both a glass trap and one of such a large volume. The flask was replaced by one of high-impact plastic of lower volume (250 ml). The tube leaving the trap was placed outside a nearby window to allow the unburned hydrogen to disperse.

2. The Jet

The material used to fabricate the jet was found to be critical in determining the sensitivity and overall performance of the detector. The first jet used consisted of Pyrex brand glass tubin (3.5 cm x 0.6 cm o.d.) wrapped with platinum foil and attached to the base of the detector with a 1/4" Swagelok to 1/8" pipe stainless steel adaptor. The tube was held firmly using a 1/4" graphite ferrule. The temperature at the tip was found to be sufficiently high to melt the glass tube and cause constriction (800°) and the flame was extinguished within one hour. Replacement of the jet required cooling the entire detector before removal and reheating before subsequent use with a new jet--a process requiring several hours.

Copper tubing proved entirely unsuitable due to immediate oxidation at this temperature (the inner wall of the jet was in constant contact with molecular oxygen). Small particles of the oxide were constantly observed as "spiking" on the strip chart recorder as they were blown from the jet tip inside the operating detector.

Stainless steel produced a longer-lived jet than glass, however, extensive oxidation rapidly made the jet useless.

In all cases it was found that the inside diameter of the jet must be greater than 2.5 mm in order for the unit to maintain combustion. Due to its smaller inside diameter, the jet described by Aue and Hill was found to be useless in this smaller model. It is recommended that the jet be fabricated out of Vycor brand tubing covered with platinum foil, or gold plated metal tubing.

3. The Ignitor

The model airplane "glo-plug" described by Aue and Hill proved unsuccessful when used as an ignitor in this HAFID. This, presumably, was due to the higher linear velocity of the gas in the smaller diameter detector, causing the heating element to maintain a lower temperature than required to ignite the hydrogen-oxygen mixture. In order to maintain a high temperature, a heavier gauge heating element had to be used. Several substances were tested as filaments, such as tungsten, tantalum, platinum, and nichrome wires. Tungsten wire proved to be more resistant to oxidation, although more brittle and more difficult to coil, than tantalum wire (0.020"). The rapid oxidation of tantalum was prevented by covering the wire with a fused coat of aluminum oxide/sodium silicate, but the added bulk of the filament required excessive amounts of current to cause ignition. Platinum was found to be unacceptable since it could only be used as a very fine wire due to its relatively high conductivity and oxidation became a problem because of this small diameter of the wire. Nichrome wire (0.020") proved to be superior due to its resistance to oxidation, and the filament was powered by a filament transformer providing 12 VAC at 12 amperes. A momentary switch was placed in the 117 VAC power line leading to the transformer (Figure 4).

In order to prevent corrosion of the filament and interference caused by the filament being present in the flame, an ignitor assembly had to be designed which would allow removal of the filament from the flame after ignition. A three-inch length of 1/4" galvanized pipe was threaded at one end and attached to a threaded hole in the side of the lower portion of the detector (Figures 1 and 2).
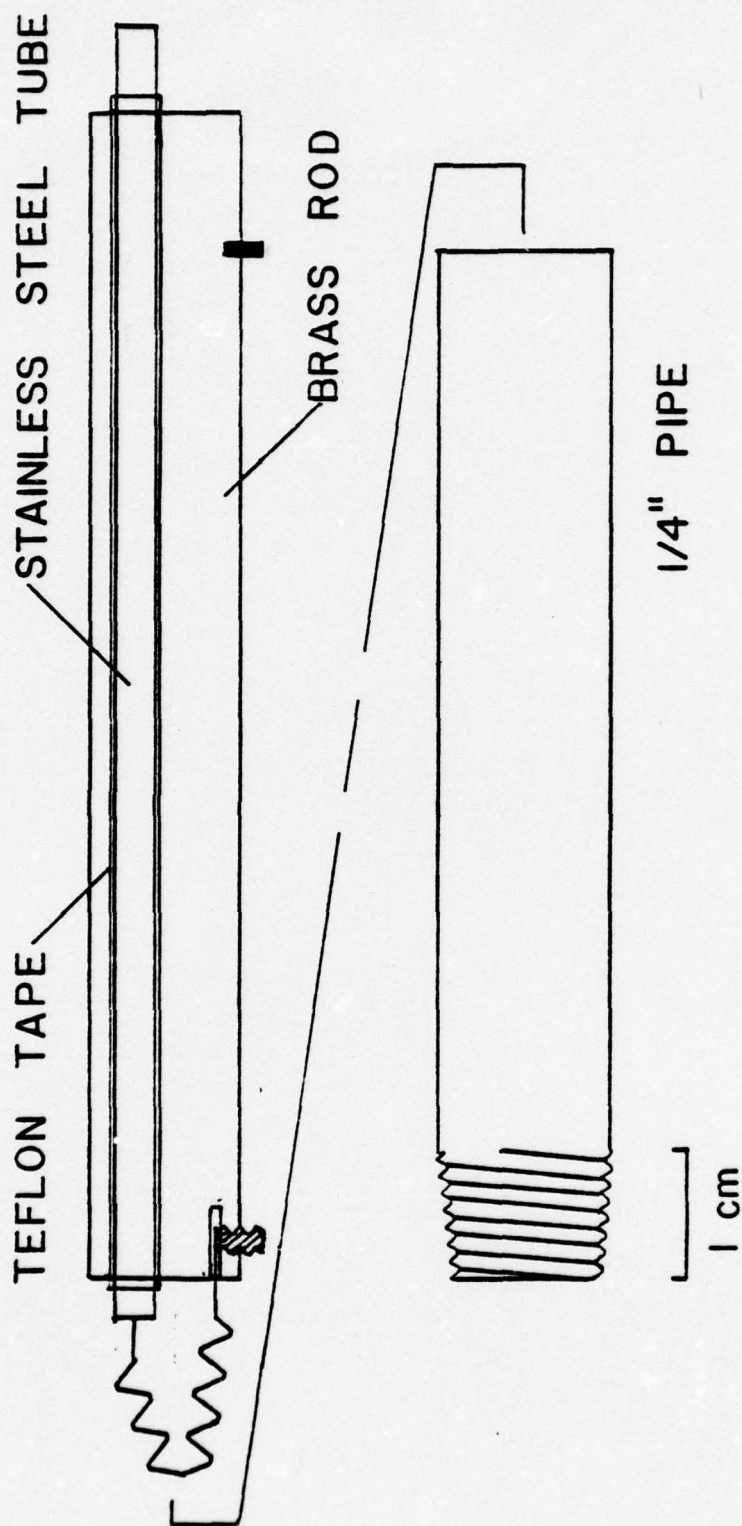
FIGURE 2. THE IGNITOR ASSEMBLY. THE BRASS ROD SLIDES INSIDE THE 1/4" PIPE FOR EASY REMOVAL OF THE FILAMENT FROM THE FLAME.

A piece of brass rod, machined to slide inside the pipe, was drilled 3/16" as shown in Figure 2. A small hole was also drilled and fitted with a set screw perpendicular to the bore to accommodate one end of the filament. The other end of the filament was crimped inside one end of a 12 cm length of 1/8" o.d. stainless steel tubing. This tube was insulated on the outside with Teflon tape and inserted into the 3/16" hole in the brass rod. This assembly provided the necessary ignition system with one lead from the 12 VAC source attached to the stainless steel tube and the other lead grounded.

4. The Platinum Electrode

The first electrode consisted of a 20 cm length of 18 gauge platinum wire with a 1 cm loop formed at the lower end. The wire was attached to the top of the detector by wrapping the upper 5 cm with Teflon tape and inserting this insulated section of the wire through a 1/8" brass Swagelok union. The union was rethreaded at one end to allow it to be screwed into a thread hole at the top of the detector (Figure 1).

The electrode proved to be unsatisfactory since its small diameter was easily vibrated to produce baseline noise. A new electrode was made from a solid platinum rod, 150 nm long and 3 mm in diamter. The lower 2 cm of the rod was flattened using a file and bent at a 90° angle to serve as a "loop."

Studies directed at lowering baseline noise led to the conclusion that the loop should have a large surface area, but also should not restrict the flow of hydrogen through the detector in any way. The best electrode tested consisted of the platinum rod having a 1 cm loop attached at the lower end. This loop was covered with

a small disc of platinum gauze (40 mesh).

The electrode potential was supplied using a 240 VDC Barber Coleman battery box as described by Aue and Hill. Lowering the voltage to 80 volts decreased the detector's sensitivity slightly and increasing the potential to 800 volts showed no pronounced increase in sensitivity. A lower noise level was obtained when a negative potential was applied to the electrode (positive ground).

5. Heating and Insulation

Heating was accomplished using four 200 watt heating cartridges connected to two variable voltage transformers. Two were used to maintain a detector temperature of 240°C and the other two were used to accelerate heating time to this temperature (monitored via an iron-constantan thermocouple buried in the detector base).

The entire detector was enclosed in a 32 x 13 cm clay pipe covered with a block of heat resistant material. The base of the detector was screwed to a cast iron housing so that the ignitor was positioned at the base of the clay pipe, as shown in Figure 3. The wiring diagram for the system is shown in Figure 4.

6. Gas Flow Rates

Hydrogen entered the detector at the base through a 1/4" duct covered with a single layer of platinum gauze. The optimum flow rate after repeated trials was found to be 420 ml/min. The flow rate of oxygen was 170 ml/min., the minimum necessary to support combustion when mixed with helium at a flow rate of 40 ml/min.

Samples greater than 5 μl in volume, including those containing water, were found to extinguish the flame unless the
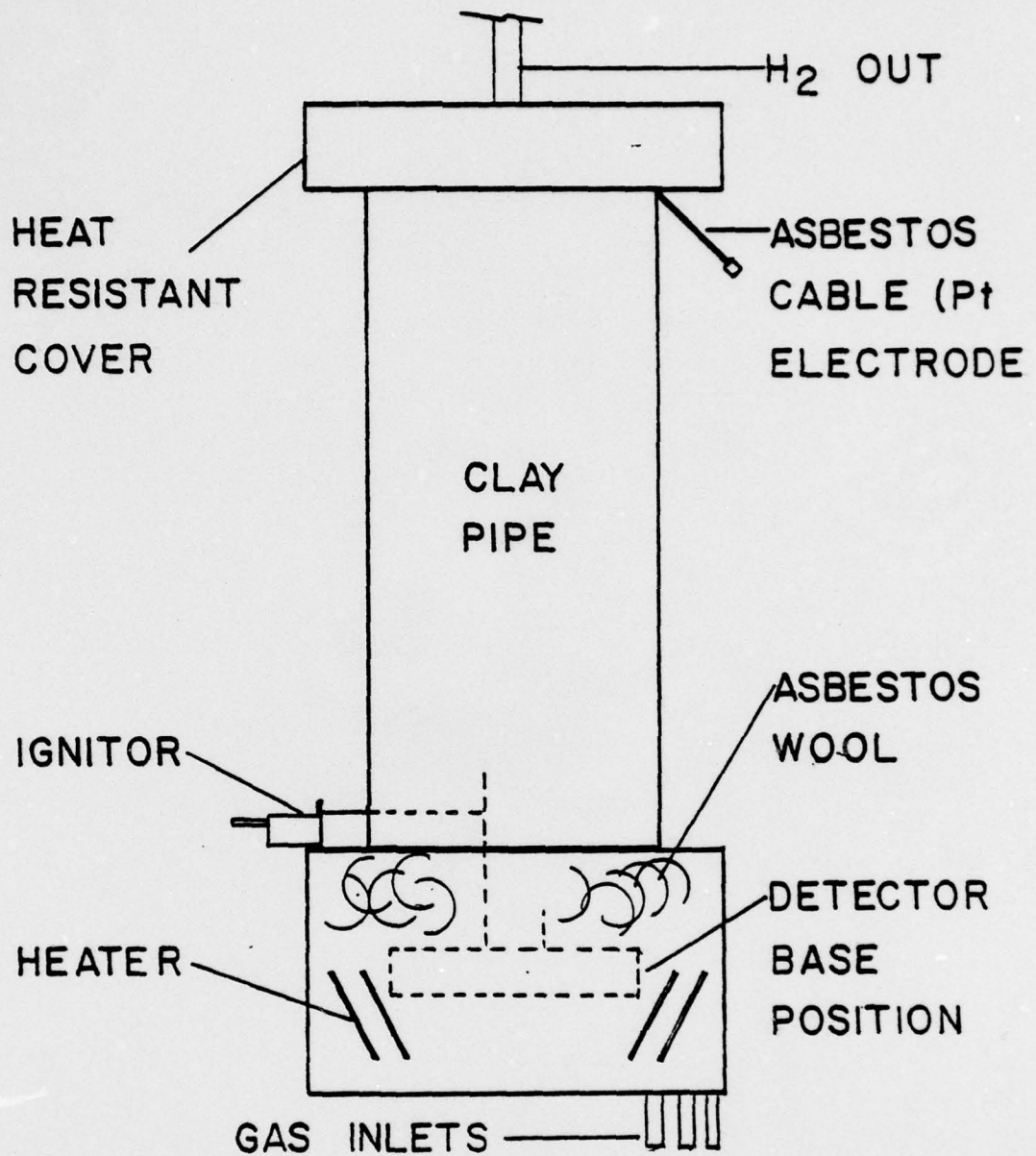
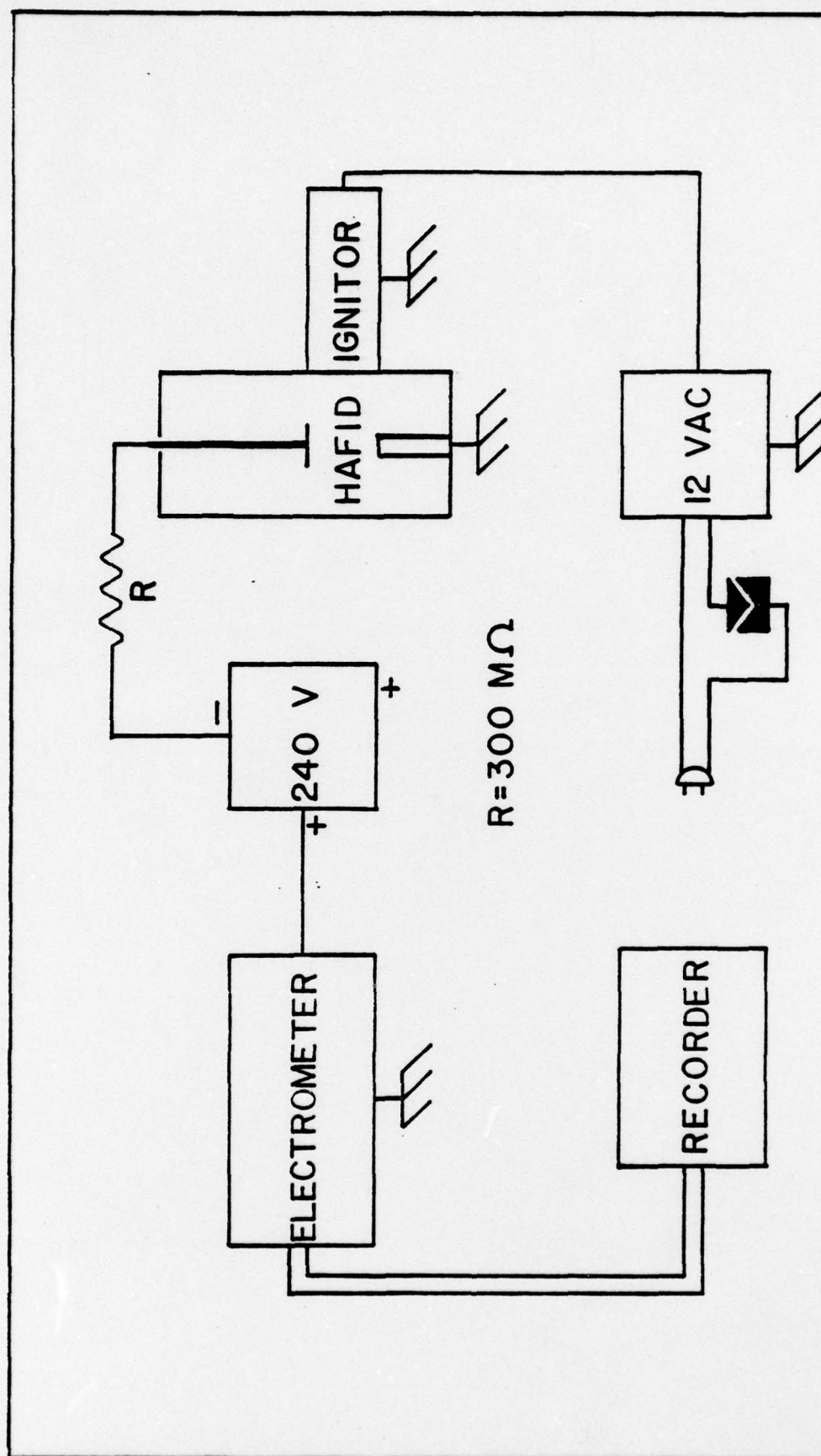FIGURE 3. MOUNTED HAFID SHOWING HEATER POSITION AND INSULATION.

FIGURE 4. WIRING DIAGRAM.

oxygen flow rate was raised 10 to 20 ml/min. higher than the above-stated 170 ml/min. rate. Diluting the oxygen with air extinguished the flame in all cases.

7. The Gas Chromatograph

A gas chromatographic oven taken from a Hewlett Packard 700 gas chromatograph and equipped with a glass analytical column containing 5% SE-30 on Gas Chrom Q was connected to the detector with a 1/16" stainless steel tube wrapped with asbestos cord covered with a 6' x 1/2" heating tape (240°C). The electrometer, a Barber Coleman Model #3044, was connected to a Barber Coleman battery box. The strip chart recorder was a Bristol Dynamaster with a 1 mV range.

It was found that the detector, being very sensitive to external vibrations, had to be isolated from the oven since the fan runs constantly with this particular gas chromatograph.

8. Detector Operation

The routine procedure used to prepare the HAFID for operation was as follows:

The assembled detector was first brought to a temperature of about 300° using the four heating elements described before. Two of the heaters were then shut off and the two remaining detectors were used to maintain a temperature of 240° at equilibrium. This required about 1.5 hr.

The hydrogen was then adjusted to its optimum flow rate and the detector was flushed out for at least 20 minutes before ignition was attempted. The flame was ignited by pressing the momentary switch (Figure 4) for a 5-second period, turning on the oxygen regulator, and

continuing pressing the switch for an additional 5 seconds. After
5 minutes the ignitor was pulled out of its housing slowly to a
distance of one inch and ignition was verified by touching the hot
effluent tube leading to a water trap.

When determining the optimum flow rates, the oxygen was
first set at a low flow rate, ignition was attempted and, if
unsuccessful, the oxygen was turned off completely for at least
20 seconds before attempting reignition. During all ignition
procedures the helium flow rate was maintained at 40 ml min^{-1}.
Flow rates were checked every 7 - 10 days of use since any
variance either caused the flame to extinguish or resulted in
unexplained explosions.

During the course of this research, explosions occurred
and, in many cases, the trap exploded. Flow rates must be optimized
and hydrogen must be allowed to flow freely without any obstruction
to minimize this hazard. The trap must be made of high impact
plastic, never glass, and the smaller the volume the less deafening
the explosion.

After the stable baseline was achieved (about 2 hrs), the
instrument was ready for use. Additional noise reduction was
accomplished by incorporating a 300 megaohm resistor in the circuit,
as shown in Figure 4.

Major adjustments to the detector, such as repositioning the
electrode or cleaning the jet, required cooling the detector and
repeating the entire procedure.

9. Trouble Shooting

The major problems encountered in operating the HAFID together

with their probable causes are listed below:

a) No response on strip chart recorder.

This was found to be caused by the platinum electrode being shorted to the detector barrel when the detector was lit. Insufficient insulation provided by the SE-30 coating also lowered detector response. The primary cause, however, was found to be due to an extinguished flame.

b) Explosion.

This was caused by improper flow rates or an obstruction in the hydrogen path. Late ignition, or attempted reignition after the flame went out, always produced an immediate explosion.

c) Flattened peaks.

Insufficient heating of the 1/16" stainless steel line cause this problem.

d) Spiking.

This was caused by extensive oxidation of the jet.

e) Flame extinguished with injected sample.

The reasons for this problem was too large a sample size, too high a helium flow rate, insufficient hydrogen or oxygen flow rates, or a combination of these.

C. Experimental Results

All electrode distance measurements required one day each after optimum operating conditions were found. Problems encountered in designing the crude instrument, together with constant alterations made to arrive at the final design, required much of the time allotted for this study. Due to their relatively high toxicity, the analysis

of organotin compounds was concentrated upon for the remainder of the research.

Tetra-n-butyl tin (TBT) and tributyl tin chloride (TBTC), the standards, were obtained from the Aldrich Chemical Co., Milwaukee, Wisconsin, and used without further purification.

The sensitivity of the detector was found to be a function of the distance between the jet and the platinum electrode. The optimum distance for the detection of the organotin compounds was determined by injecting 1 µl samples of a 1% solution of TBT in hexane and in tetradecane, varying the distance from 20 mm to 60 mm. The optimum electrode distance was found to be 55 mm for TBT (Table 10) with a relative sensitivity 2200 times greater than that of tetradecane. The sensitivity relative to tetradecane increased with the injection of smaller quantities of TBT. It was also noted that even though peak contours were not strictly reproducible, the areas under the peaks were reproducible.

The response to TBTC was found to be about the same as for TBT and because of uncorrected baseline noise, the lower limit of detection was 5 ng of TBR and TBTC, corresponding to 1 ppm in a 5 µl injection.

Water samples containing TBT and TBTC contaminated with C_{12}, C_{14}, C_{16}, and C_{18} hydrocarbons were prepared by shaking distilled water (400 ml) in a 500 ml sepratory funnel with 0.5 ml of the organotin compounds and 3 - 5 ml of each of the hydrocarbons, dodecane, tetradecane, hexadecane and octadecane.

The mixture was allowed to stand for 48 hours prior to analysis; the water samples were then drained from the bottom of the

TABLE 10

Relative Selectivities of Tetra-n-butyl Tin Versus

n-Hexane and Tetradecane with Increasing Distance

Between the Detector Jet and the Negative Electrode

| | Sensitivity | |
Distance (mm)	Relative to Hexane[a]	Relative to Tetradecane
20	1[b]	1[b]
25	1[b]	8
30	31	60
35	630	500
40	425	500
45	840	720
50	760	1570
55	843	2200
60	1028	1380

[a]Inconsistency in the data when TBT is compared to hexane is due to the fact that hexane burns at a much higher rate than tetradecane and the initial flash inside the detector produces an inconsistent potential across the electrodes.

[b]The detector functioned as a normal flame ionization detector.

separatory funnel through a Teflon stopcock. These samples were analyzed using the HAFID and the results compared with those obtained using the normal flame ionization detector. See Figures 5 and 6 for a comparison of the chromatograms.

The retention times of the tin compounds are approximately the same as those of the dissolved hydrocarbons and, since the hydrocarbon content of the water samples was relatively high, no detection of either TBT or TBTC was accomplished using the standard flame ionization detector, Figure 5.

Using the HAFID, however, the organotin compounds were readily detected in the low ppm range without the need of any preconcentration step, Figure 6. All results were found to be reproducible. Although injection of water samples directly into the instrument gave excellent results, if detection in ppb or lower ranges are desired, further improvements in the conditions responsible for the base line noise in the instrument, or the use of a preconcentration step will be necessary.

V CONCLUSIONS AND RECOMMENDATIONS

To date no feasible method has been developed for the routine analysis of trace organometallic compounds in water. Hundreds of researchers around the world are working on this problem and many are interfacing atomic absorption spectrophotometers with gas and liquid chromatographs. We, however, encountered so many problems with the atomic absorption spectrophotometric apparatus that we recommend that further studies be concerned with the development of the gas chromatographic method utilizing the hydrogen enriched flame ionization detector first introduced by Aue and Hill (3).
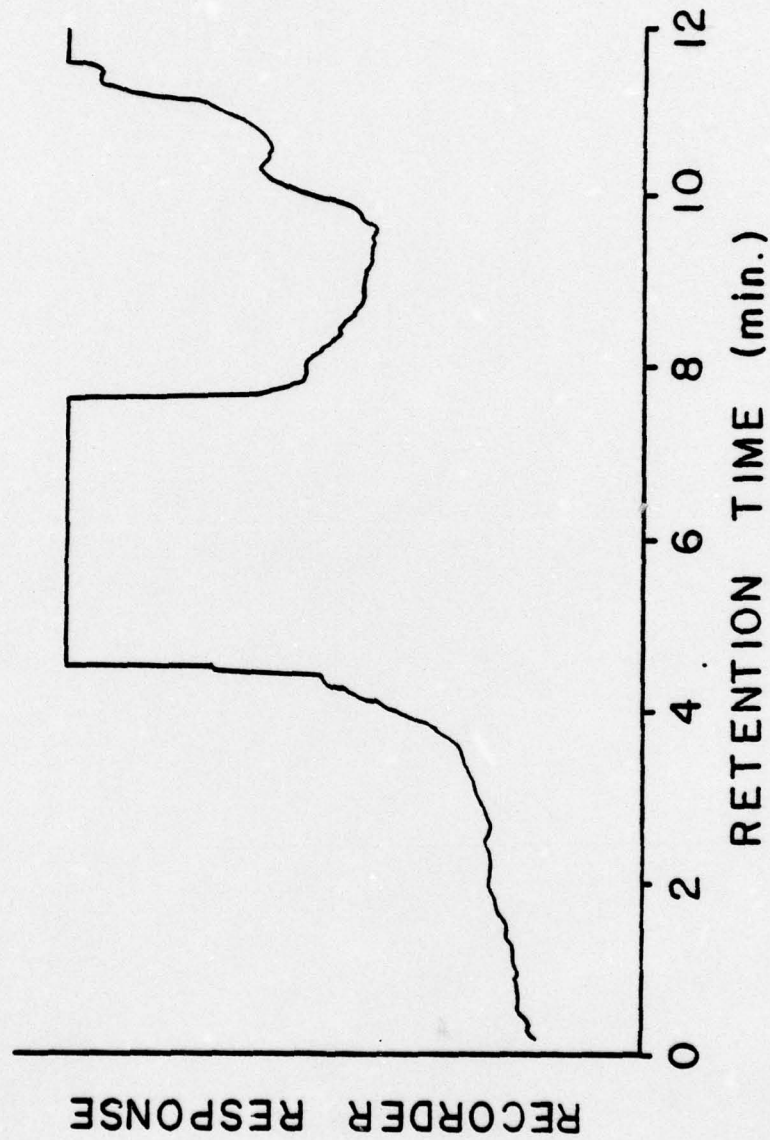
Fig. 5. Gas chromatogram obtained by injection of 1 μl of water containing TBT, TBTC, and a mixture of hydrocarbons on a column of 5% SE-30 on Gas Chrom Q using standard flame ionization detector.
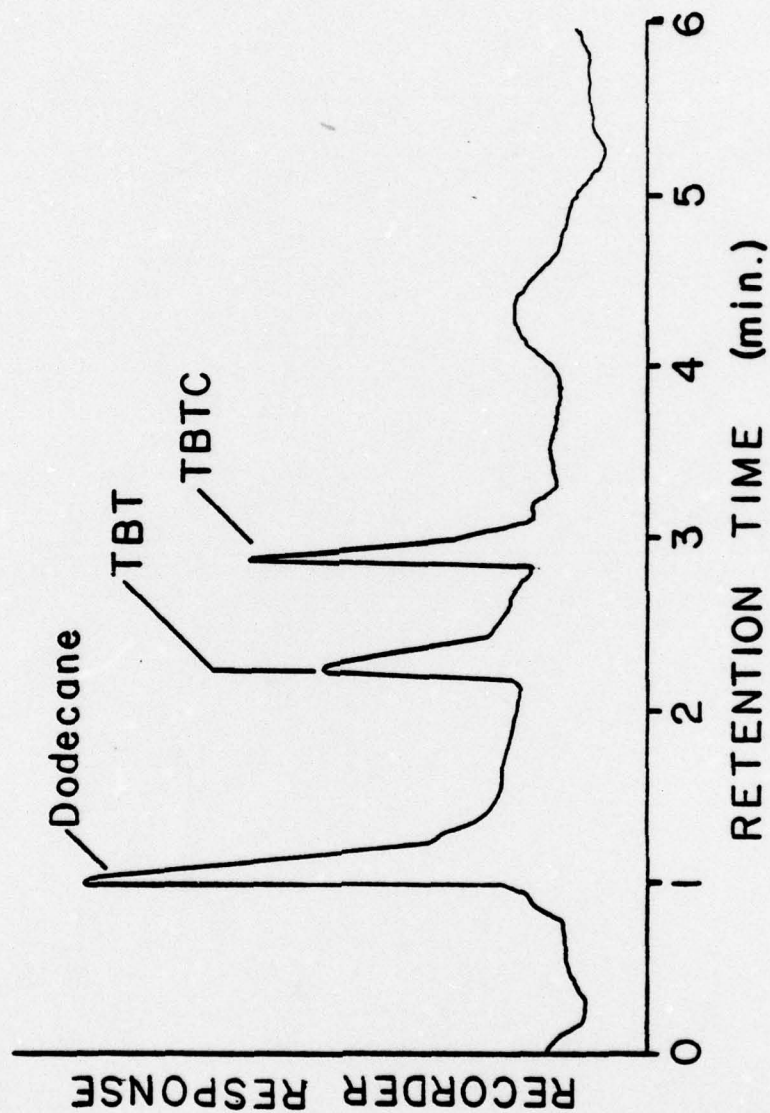
Fig. 6. Gas chromatogram obtained by injection of 1 µl of water containing TBT, TBTC, and a mixture of hydrocarbons on a column of 5% SE-30 on Gas Chrom Q using hydrogen atmosphere flame ionization detector (HAFID).

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